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TITLE: CONDUCTIVE NONUNIFORM HOLLOW FLAT PLATE

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ABSTRACT:

PURPOSE: To realize a fuel cell of high performance with small internal resistance by setting porosity of a part into contact larger than porosity of a part not into contact with an electrolytic layer of a conductive hollow flat plate used in a solid electrolyte fuel cell.

CONSTITUTION: In a conductive hollow flat plate for constituting a flat plate type electrode substrate having through ports 30-3 in the inside formed of electrode material, a part 30-1 of enriching porosity and a part 30-2 of enriching minuteness are provided in a supporter 30. A layer of an electrolyte 21 and a fuel pole 22 is formed by flame spraying method in a surface of the part 30-1, to obtain a single cell. In an opposite side surface, a collector

layer 23 is formed by flame spraying lanthanum chromite, and in the other part, a fine protecting layer 24 of alumina is formed. Thus by reducing passing resistance of gas in a part of high porosity and improving conductivity due to low porosity in a part unnecessary for gas to flow, a fuel cell of excellent performance on the whole can be economically manufactured.

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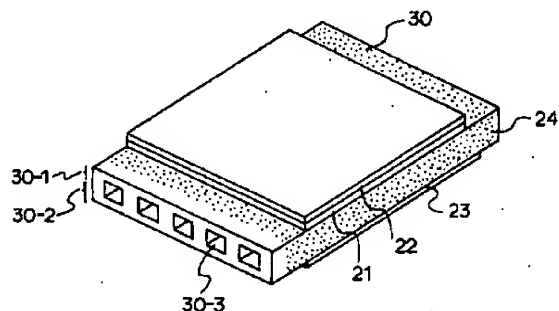
(54)【発明の名称】 導電性不均一中空平板

(57)【要約】

【目的】内部抵抗の少ない高性能の固体電解質燃料電池を実現することのできる導電性中空平板を提供すること。

【構成】上記目的は、電極材料から作製され、内部に貫通口を有する平板型電極基板を構成する導電性中空平板の片面に電解質層と電極層とを積層してなる固体電解質燃料電池単セルに用いる導電性中空平板において、該中空平板の電解質層に接触している部分の多孔度が電解質層に接触していない部分の多孔度よりも大きいことを特徴とする導電性不均一中空平板とすることによって達成することができる。

図3



【特許請求の範囲】

【請求項1】電極材料から作製され、内部に貫通口を有する平板型電極基板を構成する導電性中空平板の片面に電解質層と電極層とを積層してなる固体電解質燃料電池単セルに用いる導電性中空平板において、該中空平板の電解質層に接触している部分の多孔度が電解質層に接触していない部分の多孔度よりも大きいことを特徴とする導電性不均一中空平板。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は固体電解質燃料電池の単セルの支持板となる導電性中空平板に係り、特に、内部抵抗の少ない高性能の固体電解質燃料電池を実現することができる導電性中空平板に関する。

【0002】

【従来の技術】固体電解質燃料電池(Solid Oxide Fuel Cell; 以下、SOFC と略称する)は、酸素イオンの伝導性を有する固体電解質の両側に空気極と燃料極とを配置した構造を基本とするもので、空気極側に酸素ガスや空気を、燃料極側に水素ガス等を供給することによって、酸素イオンが固体電解質を伝導して水素ガスと反応し、この反応に伴う電流を各電極から取り出すことで発電を行っている。従って、固体電解質は酸素イオンの伝導性に優れているとともに、酸素や水素ガスの透過を防止し得る必要があり、緻密な膜であることが要求される。しかし、固体電解質の導電率は、1000℃においても他の構成材料に比べて小さいので、発電で得た電流を取り出す際の電圧降下を抑えるためには、固体電解質の膜を50~100μm程度の薄い膜とする必要がある。一方、各電極には、各ガスが固体電解質と電極との接触部に容易に到達できるように、多孔質とすることが要求される。このように、固体電解質は緻密な薄膜とし、該固体電解質膜の両側に多孔質の電極を形成する必要がある。

【0003】しかし、このような薄膜構造のセルは機械的な強度が不十分であるので、実用的には、図1の従来例に示すように、多孔性で不活性な物質、例えばカルシア安定化ジルコニア、からなる管13を支持体とし、この上に空気極3、固体電解質2及び燃料極4の薄膜を重ねて形成する方式が提案されている(ウエスチングハウス社)。しかし、この方式においては、発電時の電流 I が図に示したように電極の薄膜中を流れて隣接するセルに流れるため、この部分での電圧降下が無視できないものとなり、必ずしも十分な発電特性が得られないという問題があった。また、円筒状の多孔質管を支持体として使用し、複数の単セルを組み合わせて発電部を構成するので、円筒の内外における空間部の占める容積が大きくなり、この結果、発電部全体の容積が大きくなるという問題もあった。

【0004】以上述べたような従来技術の有する問題点を改善するために、本発明者等は、先に、支持体の材料

を空気極材料とし、積層した場合の死容積を減少させるために、形状を2枚の平板の間に複数の連結部を設けた中空状とし、この表面に発電部を形成する方式を提案した(特開平5-36417)。この提案は図2に示すような構造のセルであり、(a)はその外観図、(b)は(a)のB-B'断面を示した図である。この単位発電セル20では、空気極材料によって薄板状で複数の貫通口25-1を有する中空状の支持体25を作製し、その表面に固体電解質21、燃料極22の各層を形成し、燃料極22の反対側の表面に集電層23を設けてある。固体電解質21及びその上面に形成する燃料電極22は貫通口25-1に交差する方向に横長となる形状として複数配列する。また、集電層23は燃料電極22の反対側に支持体25のほぼ全面を覆うように設ける。ここで、支持体25は空気極材料として通常使用されているLaSrMnO₃を用いて作製し、固体電解質21や燃料電極22の各層は何れも溶射法によって作製し、固体電解質21の層はイットリア安定ジルコニア(イットリア含有量は8モル%、略称YSZ)、燃料電極22はNiOとYSZの混合粉末で形成されるサーメットを用いて、それぞれ50~200μmの厚さに作製する。また、固体電解質21の層の反対側の面に設ける集電層23も、溶射法によってNi-Al₂O₃やLaCrO₃の層を形成する。また、これらの層を設けない部分には、必要によって、ガスの透過を防止するために、アルミナ等によって緻密な表面保護層24を形成する。

【0005】

【発明が解決しようとする課題】しかしながら、上記のような構成にすると、支持体の材料となる電極に対応したガスは支持体内の貫通口25-1を流れることになるので、支持体の両端部におけるガスの気密性を確保しておくだけでガスシール性を確保することができるとは、この場合には、電極材料からなる支持体は単セルを支えるとともに、複数のセルを直列接続した際の圧迫力にも耐える必要があり、ある程度の機械的強度が必要となる。一方、このような強度の確保だけでなく、支持体は内部にガスを通し厚さ方向には電流を流す必要があるため、そのようなガスの通過抵抗の増加を抑えるとともに、支持板そのものの電気抵抗も極力抑える必要があった。また、重要なことは、YSZを形成した表面へのガスの供給が十分に行われることであり、このためには、その部分が多孔性に富んでいることが必要である。この方式のSOFCで用いられるような支持体の製造方法としては押し出し成形法があるが、この方法では成形体全体が均一な物性となったものが作製され、反応に必要な多孔性を重視して支持体を形成すると、成形体全体が多孔性に富んだものになってしまう。

【0006】一般に、電極の多孔性としては30%前後の値が要求されているが、焼結体の強度は多孔度とも関連しており、多孔度の増加につれて低下するので、このような多孔度を持った支持体を作製すると、その支持体の

機械的な強度は低いものになってしまう。このような強度の不足を補うためには支持体の厚さを増すことが考えられるが、板の厚さを増加させると板の電気抵抗が増し、中空基板を使用したにも拘らず、単セルの特性を十分に発揮できないという重大な欠点があった。

【0007】すなわち、固体電解質を形成した薄板は電極として作用する部分であり、多孔性が必要であるが、これ以外の部分については導電部、及び機械的強度の確保の付与部としてのみ作用すれば良いので、緻密な焼結体として、高い導電性を与えるとともに、板の強度も高くすることが考えられる。このような対策を施すと、中空板を使用した方式の SOFC の発電特性が向上するが、このように多孔性が部分的に異なる不均一な中空板の製造方法はこれまで確立されていなかった。

【0008】本発明の目的は、上記従来技術の有していた課題を解決して、内部抵抗の少ない高性能の固体電解質燃料電池を実現することのできる導電性中空平板を提供することにある。

【0009】

【課題を解決するための手段】上記目的は、電極材料から作製され、内部に貫通口を有する平板型電極基板を構成する導電性中空平板の片面に電解質層と電極層とを積層してなる固体電解質燃料電池単セルに用いる導電性中空平板において、該中空平板の電解質層に接触している部分の多孔度が電解質層に接触していない部分の多孔度よりも大きいことを特徴とする導電性不均一中空平板とすることによって達成することができる。なお、上記中空平板は、一方を多孔体、他方を緻密体となるように調製したスラリーから形成したテープキャスト体の積層と焼結とによって容易に得ることができる。

【0010】

【作用】従来の円筒型支持管を使用する SOFC では、多孔質チューブ上に固体電解質薄膜、各電極等を積層していた。このような円筒型では次のような問題点があった。(イ) 発電電流が電極内を面に沿って流れ、電流の通路が長くなるため、内部抵抗がおおきくなること、(ロ) 支持体が円筒であるためにこれらを複数接続した場合、発電部が大きくなり、出力密度に限界が生じること。

【0011】このような欠点を解決するために、電極材料によって支持体を作製し、かつ、支持体の形状を中空平板状としてこの表面に発電部を形成する方式を提案し、その結果、電流は電極に対して垂直に流れるようになり、従来の円筒型で見られたような電流の電極内の横方向の流れを防止することができ、放電特性の改善と発電部の小型化が達成された。しかし、従来、このような中空平板状の支持体は全体の物性が均一な材料で作製されており、この方式のセルの性能向上に効果を有する、発電部形成部のみを多孔性とした支持板の作製は行われていなかった。

【0012】これに対し、本発明構造の導電性不均一中空平板とすることによって、上記従来技術が有していた問題点がすべて解消され、部分的に多孔性の異なる中空平板を容易かつ経済的に作製することができ、これによって内部抵抗の少ない高性能な SOFC を実現することができる。

【0013】

【実施例】以下、本発明の導電性不均一中空平板について、実施例によって具体的に説明する。

【0014】図3に本発明の中空状の空気極基板の構造を示す。ここで、30は支持体、30-1は多孔性に富んだ部分、30-2は緻密性に富んだ部分、30-3は貫通口を示す。このような中空状平板の多孔性に富んだ部分30-1の表面に電解質21と燃料極22の層を形成して単セルを作製した。これらの層の形成は、従来技術の場合と同様に、溶射法によって行った。また、電解質形成面の反対側にランタクロマイトを溶射して集電層23を形成した。また、これらの薄膜を形成した部分以外には、アルミナによって緻密な表面保護層24を形成した。図5に、本発明による中空状空気極基板を使用して作製した単セルの断面図を示す。

【0015】次に、上記中空状平板の作製手順について説明する。この実施例では、空気極材料として一般的に広く使用されているペロブスカイト構造を有する $(La_{1-x}Sr_x)_yMnO_3$ ($0 \leq x \leq 0.6$, $0 \leq y \leq 0.2$) を取上げ、この中から組成 $La_{0.8}Sr_{0.2}MnO_3$ および $La_{0.9}Sr_{0.1}MnO_3$ 、平均粒径 $1 \sim 3 \mu m$ の原料粉末を使用した。また、中空平板の作製法としてはシート成形体を熱融着させる方法を用い、熱融着させたグリーン体を焼結することによって中空状の物体を得た。シート成形体はドクターブレード法によって作製し、これに必要なスラリーは下記の混合比(重量)で調合した。

【0016】

原料粉末	100
結合剤	10~15
可塑剤	5~10
溶媒	200

なお、上記の結合剤としてはポリビニルブチラール、可塑剤としてはフタル酸ブチル、溶媒としてはイソブチルアルコールを使用した。ここで、結合剤の量と可塑剤の量とに範囲を設けたのは、原料粉末の粒径が異なるとその表面積も変わり、同一の使用量ではスラリーの性状に差が生じるので、これを適切に調節するためである。この他に、スラリーの性状に応じて分散剤と消泡剤とを少量添加した。このような混合物を約24~48時間ボールミルによって攪拌した後、減圧下で脱気し粘度を調整し、この後、ドクターブレード装置によってシート成形体を得た。

【0017】このようにして作製した成形体を約400℃において脱脂し、その後1200~1400℃で焼結させ、焼結

特性を求めた。一例として、各温度で2時間焼結させたときの焼結特性を図4に示す。収縮率は、焼結温度と原料粉末の粒径とに関係しており、焼結温度が高いほど大きな収縮を示すが、ある温度以上の領域では一定の値に収束する傾向がある(a)。収束する値は原料粉末の粒径に依存し、粒径の小さい方が収縮率が大きくなる。一方、収縮率と焼結体の密度との関係を見ると、これらはほぼ直線の関係になることがわかる(b)。

【0018】一方、これらと同様の収縮特性を有し、密度のみを変えた焼結体を得るため、ドクターブレード法で使用するスラリー中に所定量の炭素粉末を混入させた。添加する炭素粉末は粒径1~3 μm の粉末で、添加量は原料粉末に対し10~30重量%とした。スラリーを上記と同様の方法で調製し、シート成形を行い、焼結特性を求めた。収縮率は炭素の添加によって殆ど影響されなかったが、焼結体の密度は炭素の添加によって変えることができた。炭素の添加によって密度は低下し、焼結体の多孔度の向上を図ることができた。

【0019】次に、上記で得たシート成形体を所定の大きさに切断した後、加熱、加圧し、中空状の外観を有するシート融着体を作製した。なお、このときの加熱・加圧条件はシートの軟らかさによって変える必要があるが、概ね70~80℃、30~70kg/cm²の条件内で行った。電解質を形成する面には炭素混入シートを配置し、中空体の形状は各層に重ねるシートの形状を選択することで任意の形とすることができた。なお、この際考慮すべきことは、焼結時におけるシート成形体の収縮であり、このような収縮を見込んで所定の大きさの焼結体となるように融着体を作製した。具体的には、図6に示したように、シートと中間連結部(b)に炭素混入シート(a)を重ねて、中空状平板の融着体(c)を作製した。このようにして、片側が多孔性で他の面及び中間の連結部が緻密性に富んだ中空状平板の融着体を作製することができた。このように融着した中空平板を400℃において脱脂し、この後1300℃で焼結して中空平板状基板を作製した。中空平板の大きさとしては、100×150mm、厚さ5mm程度のものが作製できた。

【0020】なお、焼結の進行は使用する原料粉末の粒径と結合剤、可塑剤の添加量とによって影響されるので、これらの影響を考慮して使用原料に応じて温度と時間を適宜選定する。粒径が小さい原料は表面積が大きく、低温領域から焼結が始まるので低温・短時間の条件で焼成した(例えば、1250℃、2時間)。このように、焼成条件を原料粉末や結合剤等の添加量に依り適宜選定して焼成することで多孔性部の多孔度を30%前後とした焼結体を得、このとき、緻密性に富んだ部分の多孔度は5

~10%前後となった。なお、酸化剤極の導電率は多孔度によっても左右され、この焼結体の正味の導電率(1000℃)は以下のものであった。

【0021】

多孔性部	導電率(1000℃)	100 S/cm
緻密部	同上	150~200 S/cm

本発明の導電性不均一中空平板を用いた SOFC の動作に当っては、従来の SOFC の場合と同様に、単セルを1000℃等の温度条件下に設置し、支持体25の内側に酸化剤ガスを、外側に水素ガスを供給した。この単セルを使用した発電モジュールの構成、及び、発電モジュールにおけるガスの供給方法等については特開平5-36417に示した方法を好適に用いることができる。

【0022】

【発明の効果】以上述べてきたように、導電性中空平板を本発明構成の中空平板とすることによって、従来技術の有していた課題を解決して、SOFC の支持体に適した、多孔性が部分的に異なる不均一中空平板の簡易な作製が可能となった。具体的には、ドクターブレード法を採用し、スラリー調製時に炭素粉末を混入させることによって、収縮率の変化なしに焼結体の多孔度の制御が可能とした。多孔度を高めることにより、ガスの通過抵抗が減少し、ガスが流れる必要のない部分では多孔度を低下させたために導電率が向上して、総体的に優れた性能を有する SOFC を経済的に作製することが可能となった。

【図面の簡単な説明】

【図1】従来の円筒型燃料電池単位発電セルの構造を示す一部断面斜視図。

【図2】従来の中空平板支持体を用いた単位発電セルの構成を示す図で、(a)は外観を示す斜視図、(b)は断面図。

【図3】本発明の不均一中空平板状支持体を用いた単位発電セルの概略構成を示す斜視図。

【図4】空気極焼結体の焼結特性を示す図。

【図5】本発明中空平板状空気極基板を用いて作製した単位発電セルの構造を示す断面図。

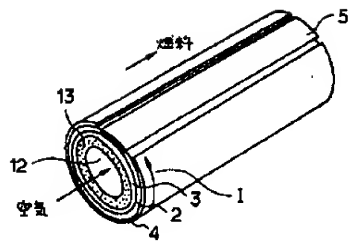
【図6】本発明中空平板状基板作製の手順を示す断面図。

【符号の説明】

1…単位発電セル、2…固体電解質、3…空気極、4…燃料極、5…集電層、12…酸化剤通路、13…多孔質管、20…単位発電セル、21…固体電解質、22…燃料極、23…集電層、24…表面保護層、25…支持体、25-1…貫通口、30…不均一支持体、30-1…多孔度の高い部分、30-2…多孔度の低い部分、30-3…貫通口。

【図1】

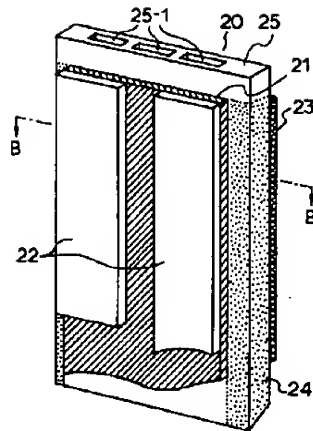
図1



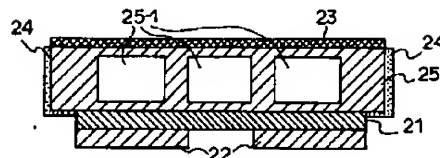
【図2】

図2

(a)

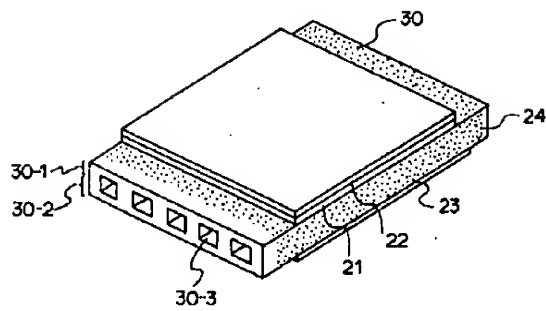


(b)



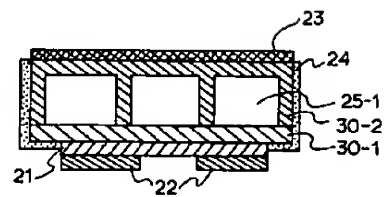
【図3】

図3



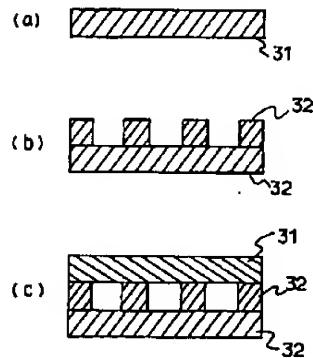
【図5】

図5



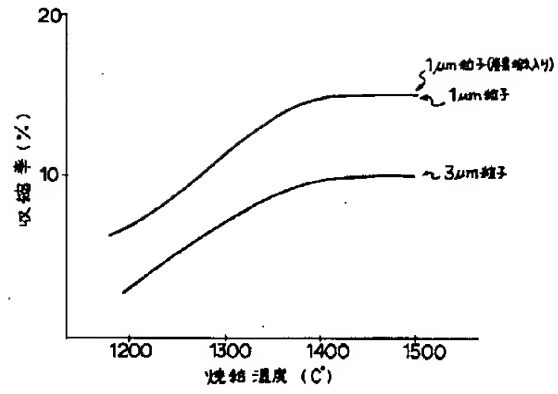
【図6】

図6

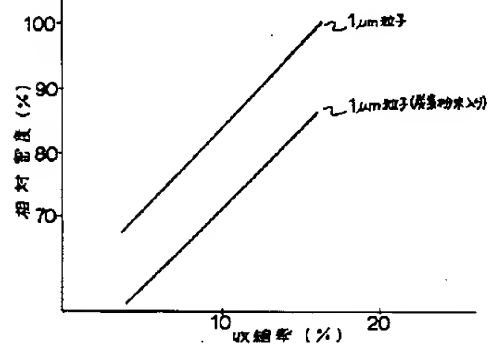


【図4】

図4 (a)



(b)



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CLAIMS

[Claim(s)]

[Claim 1] the conductive hollow which constitutes the monotonous type electrode substrate which is produced from an electrode material and has a penetration mouth inside -- the conductive hollow plate used for the solid-electrolyte-fuel-cell single cell which comes to carry out the laminating of an electrolyte layer and the electrode layer to monotonous one side -- setting -- this hollow -- the conductive uneven hollow characterized by the porosity of the portion in contact with the monotonous electrolyte layer being larger than the porosity of the portion which does not touch an electrolyte layer -- monotonous

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the conductive hollow plate used as the support plate of the single cell of a solid electrolyte fuel cell, and relates to the conductive hollow plate which can realize a highly efficient solid electrolyte fuel cell with little internal resistance especially.

[0002]

[Description of the Prior Art] By supplying oxygen gas and air to an air pole side, and supplying hydrogen gas etc. to a fuel-electrode side on the basis of the structure which has arranged the air pole and the fuel electrode on both sides of the solid electrolyte in which a solid electrolyte fuel cell (it is called SOFC for short below Solid Oxide Fuel Cell;) has the conductivity of oxygen ion, oxygen ion conducts a solid electrolyte, reacts with hydrogen gas, and is generating electricity by taking out the current accompanying this reaction from each electrode. Therefore, while the solid electrolyte is excellent in the conductivity of oxygen ion, transparency of oxygen or hydrogen gas can be prevented and to be a precise film is demanded. However, the conductivity of a solid electrolyte needs to use the film of a solid electrolyte as an about 50-100-micrometer thin film, in order to stop the voltage drop at the time of taking out the current acquired by power generation, since it is small compared with other components also in 1000 degrees C. On the other hand, each electrode is required to consider as porosity so that each gas can reach the contact section of a solid electrolyte and an electrode easily. Thus, a solid electrolyte needs to consider as a precise thin film, and needs to form a porous electrode in the both sides of this solid electrolyte film.

[0003] however, since the cell of such a diaphragm structure has mechanical inadequate intensity, it is shown in the conventional example of drawing 1 practical -- as -- the matter inactive at porosity, for example, a calcia stabilized zirconia, -- since -- the becoming pipe 13 is made into a base material, and the method which forms the thin film of an air pole 3, a solid electrolyte 2, and a fuel electrode 4 in piles on this is proposed (Westinghouse Electric Corp.) However, it sets to this method and is current at the time of power generation. I As shown in drawing, in order to flow in the cell which adjoins [be / under / thin film / of an electrode] passing / it], it became what cannot disregard the voltage drop in this portion, and there was a problem that sufficient power generation property was not necessarily acquired. Moreover, since the cylinder-like porosity pipe was used as a base material and the power generation section was constituted combining two or more single cells, there was also a problem that the capacity which the space section internal and external [cylindrical] occupies became large, consequently the capacity of the whole power generation section became large.

[0004] in order to improve the trouble which the conventional technology which was expressed above has, this invention person etc. makes material of a base material air pole material previously, in order to decrease the gas hold up at the time of carrying out a laminating, makes a configuration the shape of hollow which prepared two or more connection sections between the plates of two sheets, and forms the power generation section in this front face -- the method was proposed (publication-number 5-36417) This proposal is the cell of structure as shown in drawing 2, and (a) is the external view ((b) a). It is drawing having shown the B-B' cross section. In this unit power generation cell 20, by air pole material, the hollow-like base material 25 which has two or more penetration mouths 25-1 by the shape of sheet metal is produced, each class of a solid electrolyte 21 and a fuel electrode 22 is formed in the front face, and the current collection layer 23 is formed in the front face of the opposite side of a fuel electrode 22. Two or more fuel electrodes 22 formed in a solid electrolyte 21 and its upper surface are arranged as a configuration which becomes oblong in the direction which intersects the penetration mouth 25-1. Moreover, a collector 23 is formed so that the whole simultaneously surface of a base material 25 may be worn to the opposite side of the fuel electrode 22. Here, it produces using LaSrMnO₃ usually used as an air pole material, each each class of a solid electrolyte 21 or the fuel electrode 22 is produced by the spraying process, and, for the layer of a solid electrolyte 21, a yttria stable zirconia (a yttria content is eight-mol % and an abbreviated name YSZ) and the fuel electrode 22 are [a base material 25]. NiO YSZ It produces in thickness of 50-200 micrometers using the cermet formed in the end of mixed powder, respectively.

Moreover, the current collection layer 23 prepared in the field of the opposite side of the layer of a solid electrolyte 21 is also a spraying process. nickel-aluminum 2O3 The layer of LaCrO3 is formed. Moreover, in order to prevent transparency of gas as occasion demands, the precise surface-protection layer 24 is formed in the portion which does not prepare these layers with an alumina etc.

[0005]

[Problem(s) to be Solved by the Invention] However, since the gas corresponding to the electrode used as the material of a base material will flow the penetration mouth 25-1 in a base material with the above composition, although gas-seal nature is securable only by securing the airtightness of the gas in the both ends of a base material In this case, while the base material which consists of an electrode material supports a single cell, it is necessary to also bear the pressure force at the time of carrying out the series connection of two or more cells, and a certain amount of mechanical strength is needed. Since not only reservation of such intensity but the base material needed to pass current for gas in the through thickness direction inside, while, suppressing the increase in passage resistance of such gas on the other hand, the electric resistance of the support plate itself also needed to be suppressed as much as possible. Moreover, an important thing is YSZ. It is that supply of gas on the formed front face is fully performed, and, for that, it is required for the portion to be rich in porosity. This method SOFC Although there is an extrusion-molding method as the manufacture method of a base material which is used, by this method, that from which the whole Plastic solid became uniform physical properties is produced, and if porosity required for a reaction is thought as important and a base material is formed, the whole Plastic solid will become what was rich in porosity.

[0006] Although the value around 30% is demanded as porosity of an electrode, since porosity is related and the intensity of a sintered compact generally falls along with the increase in porosity, if a base material with such porosity is produced, the mechanical intensity of the base material will become a low thing. Although it was possible to increase the thickness of a base material in order to compensate shortage of such intensity, and the electric resistance of a board used increase and the hollow substrate when the thickness of a board was made to increase, there was a serious fault that the property of a single cell could not fully be demonstrated.

[0007] That is, although the sheet metal in which the solid electrolyte was formed is a portion which acts as an electrode and porosity is required for it, since what is necessary is to act only as a current carrying part and the grant section of reservation of a mechanical strength about portions other than this, while giving high conductivity as a precise sintered compact, it is possible [it] to also make intensity of a board high. Method which used the hollow board when such measures were taken SOFC Although the power generation property improved, the manufacture method of an uneven hollow board that porosity differed partially in this way was not established until now.

[0008] The purpose of this invention is to solve the technical problem which the above-mentioned conventional technology had, and offer the conductive hollow plate which can realize a highly efficient solid electrolyte fuel cell with little internal resistance.

[0009]

[Means for Solving the Problem] In the conductive hollow plate used for the solid-electrolyte-fuel-cell single cell which comes to carry out the laminating of an electrolyte layer and the electrode layer to one side of the conductive hollow plate which constitutes the monotonous type electrode substrate which the above-mentioned purpose is produced from an electrode material, and has a penetration mouth inside It can attain by considering as the conductive uneven hollow plate characterized by the porosity of the portion in contact with the electrolyte layer of this hollow plate being larger than the porosity of the portion which does not touch an electrolyte layer. In addition, it can obtain easily by the laminating of a tape cast object and sintering which were formed from the slurry prepared so that the above-mentioned hollow plate might serve as a porous body in one side and might serve as a precise object in another side.

[0010]

[Function] The conventional cylindrical hanger tube is used. SOFC The laminating of a solid electrolyte thin film, each electrode, etc. was carried out on the porosity tube. There were the following troubles in such cylindrical. (b) since power generation current flows the inside of an electrode along a field and the path of current becomes long -- internal resistance -- **** -- the bird clapper which it hears, and (b) Since a base material is a cylinder, when two or more these are connected, the power generation section should become large and a limitation should arise in power density.

[0011] In order to solve such a fault, the base material was produced by the electrode material, and the method which forms the power generation section in this front face by making the configuration of a base material hollow plate-like was proposed, consequently current came to flow perpendicularly to the electrode, the flow of the longitudinal direction in the electrode of current which was seen by cylindrical [conventional] could be prevented, and the improvement of an electric discharge property and the miniaturization of the power generation section were attained. However, such a hollow plate-like base material is conventionally produced with material with the whole uniform physical properties, and production of the support plate which made only the power generation section formation section porosity which

has an effect in the improvement in a performance of the cell of this method was not performed.

[0012] on the other hand, the conductive uneven hollow of this invention structure -- by supposing that it is monotonous, all the troubles that the above-mentioned conventional technology had are canceled, the hollow plate from which porosity differs partially can be produced easily and economically, and there is little internal resistance by this -- highly efficient SOFC It is realizable.

[0013]

[Example] Hereafter, an example explains the conductive uneven hollow plate of this invention concretely.

[0014] The structure of the air pole substrate of the shape of hollow of this invention is shown in drawing 3 . Here, 30 is a base material and 30-1. The portion and 30-2 which were rich in porosity The portion and 30-3 which were rich in compactness A penetration mouth is shown. The layer of an electrolyte 21 and a fuel electrode 22 was formed in the front face of the portion 30-1 which was rich in the porosity of such a hollow-like plate, and the single cell was produced. Formation of these layers was performed by the spraying process like the case of the conventional technology. Moreover, thermal spraying of the lanthanum chromite was carried out to the opposite side of an electrolyte forming face, and the current collection layer 23 was formed. Moreover, in addition to the portion in which these thin films were formed, the precise surface-protection layer 24 was formed with the alumina. The cross section of the single cell produced to drawing 5 using the hollow-like air pole substrate by this invention is shown.

[0015] Next, the production procedure of the above-mentioned hollow-like plate is explained. In this example, YMnO_3 ($0 \leq X \leq 0.6$, $0 \leq Y \leq 0.2$) which has the perovskite structure currently generally widely used as an air pole material ($\text{La}_{1-X}\text{Sr}_X$) is taken up, and it forms out of this. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, and the raw material powder of 1-3 micrometers of mean particle diameters were used. Moreover, the hollow-like body was obtained by sintering the green object which carried out heat weld of the sheet Plastic solid using the method of carrying out heat weld as a method of producing a hollow plate. The sheet Plastic solid was produced by the doctor blade method, and prepared the slurry required for this with the following mixing ratio (weight).

[0016]

Raw material powder 100 binders Ten to 15 plasticizer Five to 10 solvent As the above-mentioned binder which is 200, isobutyl alcohol was used as phthalic-acid butyl and a solvent as a polyvinyl butyral and a plasticizer. Here, since the surface area would also change and a difference would arise in the character of a slurry by the same amount used if the particle size of raw material powder differs, the range was prepared in the amount of a binder, and the amount of a plasticizer for adjusting this appropriately. In addition, according to the character of a slurry, little addition of a dispersant and the defoaming agent was carried out. After agitating such mixture with a ball mill for about 24 to 48 hours, it deaerated under reduced pressure, viscosity was adjusted, and the sheet Plastic solid was obtained with doctor blade equipment after this.

[0017] Thus, degreased in about 400 degrees C, the produced Plastic solid was made to sinter at 1200-1400 degrees C after this, and the sintering property was searched for. As an example, the sintering property at the time of making it sinter at each temperature for 2 hours is shown in drawing 4 . Although the contraction is related to sintering temperature and the particle size of raw material powder and such big contraction that sintering temperature is high is shown, there is an inclination converged on a fixed value in the field more than a certain temperature (a). Depending on the particle size of raw material powder, as for the value to converge, a contraction becomes [the one where particle size is smaller] large. On the other hand, when the relation between a contraction and the density of a sintered compact is seen, a linear relation understands a bird clapper for these mostly (b).

[0018] On the other hand, it has the same contraction property as these, and in order to obtain the sintered compact into which only density was changed, the carbon-powder end of the specified quantity was made to mix into the slurry used by the doctor blade method. It is powder with a particle size of 1-3 micrometers, and the addition was made into 10 - 30 % of the weight to raw material powder the end of a carbon powder it adds. The slurry was prepared by the same method as the above, sheet fabrication was performed, and the sintering property was searched for. Although a contraction was hardly influenced by carbonaceous addition, the density of a sintered compact was changeable with carbonaceous addition. By carbonaceous addition, density was able to fall and was able to aim at improvement in the porosity of a sintered compact.

[0019] Next, after cutting the sheet Plastic solid obtained above in a predetermined size, it heated and pressurized and the sheet weld object which has hollow-like appearance was produced. In addition, although heating / pressurization conditions at this time needed to be changed by the softness of a sheet, it carried out in general within the condition of 70-80 degrees C and 30 - 70 kg/cm². The carbon mixing sheet has been arranged in the field which forms an electrolyte, and the configuration of a hollow object was able to be made into arbitrary forms by choosing the configuration of the sheet put on each class. In addition, it is the contraction of the sheet Plastic solid at the time of sintering which should be taken into consideration in this case, and it produced the weld object so that it might count upon such contraction and might become the sintered compact of a predetermined size. Specifically, as shown in

drawing 6, the weld object (c) of a hollow-like plate was produced for the carbon mixing sheet (a) in piles in a sheet and the middle connection section (b). Thus, one side was able to produce with porosity the weld object of a hollow-like plate with which other fields and middle connection sections were rich in compactness. Thus, it degreased in 400 degrees C, the welded hollow plate was sintered at 1300 degrees C after this, and the hollow plate-like substrate was produced. As a size of a hollow plate, 100x150mm and the about [thickness 5mm] thing were producible.

[0020] In addition, since advance of sintering is influenced with the particle size of the raw material powder to be used, and the addition of a binder and a plasticizer, in consideration of these influences, temperature and time are suitably selected according to a use raw material. Since the raw material with a small particle size had the large surface area and sintering began from the low-temperature field, it calcinated on condition that low temperature and a short time (for example, 1250 degrees C, 2 hours). Thus, the sintered compact which made the porosity of the porous section 30% order by selecting baking conditions suitably and calcinating them according to additions, such as raw material powder and a binder, was obtained, and the porosity of the portion which was rich in compactness became 5 - 10% order at this time. In addition, the conductivity of an oxidizer pole was influenced by porosity and the conductivity (1000 degrees C) of the net of this sintered compact was as follows.

[0021]

The porous section Conductivity (1000 degrees C) 100 S/cm precise section Same as the above The conductive uneven hollow plate of a 150 - 200 S/cm this invention was used. SOFC It is the former if in charge of operation. SOFC The single cell was installed in the bottom of temperature conditions, such as 1000 etc. degrees C, like the case, oxidizer gas was supplied inside the base material 25, and hydrogen gas was supplied outside. About the composition of the power generation module which used this single cell, and the supply method of the gas in a power generation module, the method shown in JP,5-36417,A can be used suitably.

[0022]

[Effect of the Invention] By making a conductive hollow plate into the hollow plate of this invention composition, as stated above, the technical problem which the conventional technology had is solved and it is SOFC. Simple production of the uneven hollow plate from which porosity differs partially suitable for the base material was attained. Control of the porosity of a sintered compact was enabled without change of a contraction by adopting a doctor blade method and making the end of a carbon powder specifically mix at the time of slurry manufacture. By raising porosity, passage resistance of gas decreases, since porosity was reduced in the portion without the need that gas flows, conductivity improves, and it has the performance which was excellent on the whole. SOFC It became possible to produce economically.

[Translation done.]